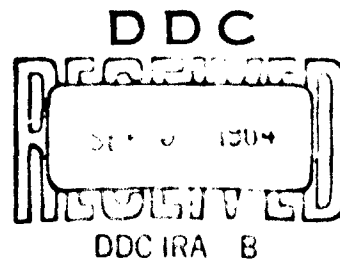175

STUDY OF ELECTRON GENERATION BY

SOLID PROPELLANT TECHNIQUE

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September 21, 1962

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Alexandria, Virginia

ABSTRACT

Electron generators functioning by combustion of a cesium nitrate-aluminum pressed charge have been developed and test-fired in an altitude chamber. Thermodynamic analysis of the combustion and nozzle-expansion process shows that about 10^{20} electrons are discharged per gram of charge, the gaseous product containing about 2 mole per cent electrons. Spectroscopic measurements of the exhaust plume at 40 mm Hg abs confirm electron concentrations of this magnitude via Stark-broadening of cesium emission lines. Details of generator operation are given, and alternate chemical systems for electron generation are discussed.

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INTRODUCTION

The importance of the ionosphere for communication is well known. The current availability of sounding rockets raises the question of the possibility of artificial generation of local short-duration ionized regions in the upper atmosphere which will interact with radio or microwaves. The significance of such effects to upper-atmosphere research and to communications techniques is obvious. Marmo, et al. (1) and Rosenberg and Paulson (2) have already described upper-atmosphere experiments in which explosive releases of cesium-containing chemicals have yielded artificial electron clouds.

An explosive release may not be the most efficient way to introduce electrons into the upper atmosphere because of the highly non-equilibrium nature of an explosion; i.e., some of the charge may not be adequately heated and/or dispersed. Also, for some experiments a continuous release with a duration of tens of seconds may be preferable to an instantaneous release. Therefore we have concerned ourselves with feasibility of continuous generation of an electron-rich plasma by a solid-propellant technique. Early results have been reported previously (3).

Free electrons rather than ions are required for strong interaction with radio or microwaves, because the charge-to-mass ratio of the latter is too small. Exhaust gases from almost any rocket contain free electrons, and if the propellant is "seeded" with alkali metals (cf. (4)), higher electron concentrations are obtainable. The problem to which we have devoted ourselves is the optimization of the electron yield per kg of charge.

Electron concentrations in the combustion chamber are readily calculated by the same well-known techniques used for analysis of any complex chemical equilibrium, if the thermodynamic parameters of the system are known and the assumption of equilibrium is valid. For the extreme temperatures and high

chamber pressures of interest here, rocket experience suggests that equilibrium
will be closely approximated in the chamber, although subsequent events during
the nozzle expansion are in some doubt. To carry out the equilibrium calcula-
tions, an IBM-7090 program is used, all relevant known energy levels of the
constituents being included. (This is the rigorous approach to the problem for
which the Saha equation is the first approximation.)

By this technique, various candidate chemical systems may be screened
on the basis of electron yield. We have arbitrarily limited our consideration
to solid ingredients to conform with logistic requirements. Clearly, one wishes
the highest flame temperature possible, since even cesium, the most readily
ionized element, is only partially ionized in the hottest known flames at
pressures reasonable for combustion (one to 50 atm). In addition to achieving
high temperature, it is vitally necessary to avoid species in the combustion
gases such as hydroxyl, atomic chlorine, atomic fluorine, etc., which form stable
negative ions. For example, in typical cesium-rich hydrogen-containing systems,
the ratio OH^-/e ranges from 10 to 100.

While our study relates to electrons produced in a combustion chamber,
it is well to remember that electrons may also be produced by photo-ionization
of exhaust gases or by virtue of extreme relative velocity between exhaust plume
and ambient. These effects are beyond the scope of this paper.

THERMODYNAMIC SURVEY OF CANDIDATE SYSTEMS

Cesium, being the most easily ionized element, should obviously be
present as a major constituent of the system. Since cesium nitrate is an ex-
cellent oxidizer, a mixture of cesium nitrate and an oxidizable metal should
yield a high flame temperature; such systems would also be free of undesirable
negative ions (except for O^-, which is much less stable than OH^-). The flame
temperature of such a system will be slightly below the boiling point (pressure-
dependent) of the product metal oxide, so metals forming stable, high-boiling
oxides are desirable. Table I shows results of calculations for a series of
such metals. These calculations were made with an IBM-7090 computer, all
known relevant equilibria being taken into account. A number of systems are
seen to be capable of yielding several mole per cent electrons. Of these,
aluminum is particularly attractive for experimental purposes because it is

available in fine powder form and has favorable handling and combustion pro-
perties. Of the metals superior to aluminum in Table I, lanthanum is pyrophoric,
beryllium is toxic, and yttrium, zirconium, and thorium are all much higher-
boiling metals than aluminum and thus should not burn as well. Also the super-
iority of yttrium may not be real but may simply be due to inaccuracy in the
vapor-pressure data for Y_2O_3. (Hafnium is another element that should give a
very hot flame but was not included for lack of data.) The low atomic weight
of aluminum gives it an advantage on a weight basis over the heavy elements,
which does not show in Table I.

The calculated properties of the aluminum-cesium nitrate system are
shown in more detail in Table II for three values of chamber pressure. The
fraction of cesium atoms ionized varies from 2.5 per cent at 68 atm to 5.4 per
cent at one atm. Since the gaseous portion of the product is about half cesium
vapor (the next largest constituent being nitrogen), the absolute concentration
of electrons is extremely high, about two orders of magnitude higher than that
achieved by seeding an oxyhydrogen flame with cesium (4). It must be noted,
however, that a significant proportion of the product of the cesium nitrate-
aluminum system is liquid aluminum oxide, in the form of micron-size droplets,
which constitute about 35 per cent by weight of the product. (Because of lack
of detailed knowledge, these calculations have ignored the possibility that
the work function of molten aluminum oxide is low enough to contribute electrons.)

For some experiments, a system producing electron-rich products free
of condensed-phase matter may be desirable, so consideration has been given to
this. Clearly, metal oxides must be avoided, so a source of high energy other
than metal combustion is required. A seeded cyanogen-oxygen flame would be
excellent except that the ingredients are not solids. Golomb and Berger (5)
have suggested that tetracyanoethylene would be a desirable solid ingredient
for such systems, when used with a solid oxidizer such as cesium superoxide
or cesium nitrate. However, our calculations show that these systems yield
much too low a flame temperature.

We suggest that the solid oxidizer hexanitroethane is uniquely suitable
for the task in hand, since it releases its oxygen with a net liberation of
energy. The cesium may be added either as cesium azide or as elemental cesium;
the former has much better handling characteristics, but the latter would have

TABLE I

PROPERTIES OF COMBUSTION PRODUCTS OF STOICHIOMETRIC MIXTURES
### OF CESIUM NITRATE WITH VARIOUS ELEMENTS AT 8.23 ATM AMBIENT PRESSURE

Element	Temp (K°)	Mole % Electrons*	Electrons/cc	Stoichiometric to
Y	4870.7	4.68	5.80×10^{17}	Y_2O_3
Th	4643.7	3.59	4.67×10^{17}	ThO_2
Zr	4563.7	3.46	4.58×10^{17}	ZrO_2
La	4405.6	2.58	3.54×10^{17}	La_2O_3
Be	4225.3	2.18	3.12×10^{17}	BeO
Al	4162.6	1.90	2.76×10^{17}	Al_2O_3
Ca	4123.4	1.70	2.48×10^{17}	CaO
Mg	3666.1	0.751	1.23×10^{17}	MgO
B	2625.8	0.0432	0.099×10^{17}	B_2O_3

*Based on gaseous portion of product.

TABLE II

COMBUSTION PRODUCTS FROM 78.32% CsNO₃ PLUS   21.68% Al

(ALL VALUES EXPRESSED AS MOLES)

Species	Pressure		
	68 atm	8.23 atm	1 atm
O	5.367	6.486	11.186
N	0.075	0.048	0.027
e	1.236	1.801	2.435
Al	3.385	4.902	6.265
Cs$^+$	1.408	1.897	2.478
O$^-$	0.171	0.096	0.043
O$_2$	1.170	1.666	1.876
N$_2$	26.383	23.907	22.369
NO	2.353	2.049	1.574
AlN	0.001	--	--
AlO	3.761	4.985	5.520
Al$_2$O	1.434	1.845	2.017
Al$_2$O$_2$	0.403	0.425	0.365
Cs	51.917	47.771	43.830
Cs$_2$	0.935	0.122	0.016
Total Gas	99.999	100.000	100.001
Al$_2$O$_3$ (liquid)	49.784	42.697	38.065
Temp (K°)	4605.3	4130.0	3715.2
Mean Mol. Wt. of Total Gas	86.59	80.65	76.50

less coolant and diluent effect per atom of cesium and would result in hotter
flames. Calculations have been made for the system:

$$3 \, C_2N_6O_{12} + 5 \, C_6N_4 + 3 \, CsN_3 \longrightarrow 36 \, CO + 23.5 \, N_2 + 3 \, Cs$$
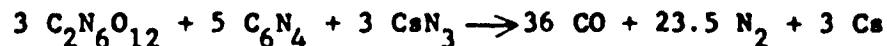
For constant-pressure combustion of 100 gm of this mixture at 1 atm,
one obtains 3.041 gm-moles of gaseous products at 3498°K with composition as
shown:

CO	57.30	mole per cent
N_2	37.40	" " "
Cs	4.28	" " "
Cs^+	0.492	" " "
e	0.492	" " "
C(g)	0.0179	" " "
N	0.0134	" " "
O	0.000399	" " "
CO_2	0.000302	" " "
NO	0.000101	" " "

Note that 11.5 per cent of the cesium is ionized, and no solid carbon forms.
On a weight basis, this system is nearly as good as cesium nitrate-aluminum
$(0.90 \times 10^{20}$ electrons/gm vs. 1.27×10^{20} electrons/gm at one atm). Also the
proportions of ingredients in the above example have not been optimized, so that
higher yields are presumably possible. An experimental approach to this system
is currently being planned.

III. ANALYSIS OF CESIUM NITRATE-ALUMINUM SYSTEM DURING NOZZLE EXPANSION

Let us consider what will happen during isentropic nozzle expansion of
the combustion products of the favored system, cesium nitrate-aluminum. The de-
crease in temperature will promote recombination, while the decrease in pressure
will promote further ionization. The competition between these effects is seen
from the following readily derivable equation which approximates the behavior of
an isentropically expanding gas following the Saha relation:

$$\left(\frac{\partial \ln\left(n_e/n_{Cs}\right)}{\partial \ln T} \right)_S = \frac{1}{2} \left(\frac{E}{RT} - \frac{\gamma}{\gamma-1} \right) \qquad (1)$$

Here, n_e/n_{Cs} is the fraction of Cs ionized (assumed much smaller than unity),

   T is absolute temperature during isentropic expansion

   E is ionization energy of Cs

   γ is specific heat ratio (assumed constant)

(In addition to the above-indicated assumptions, the effects of a $T^{5/4}$ term in the Saha equation and the variation of the total number of moles during expansion were neglected.) For cesium at 4000°K, E/RT = 11.3; the right-hand-side of the equation will accordingly be negative for values of γ smaller than 1.10, and the fractional ionization will increase during isentropic expansion. At sufficiently low temperatures, of course, E/RT will become larger than $\gamma/\gamma-1$ and the fractional ionization will pass through a maximum. For the case being considered, γ is not, strictly speaking, a constant, but the effective γ will be only slightly above unity because of the large liquid Al_2O_3 content of the stream (thermal equilibration of gas and liquid being assumed). For isentropic expansion of the $CsNO_3$:Al system from 8.23 atm to one atm, the temperature is calculated to decrease from 4130 to 3715°K; this corresponds to an effective γ of 1.053, which is well below 1.10. Hence one would expect an initial increase in ionization on expansion if the rate processes are sufficiently fast; otherwise, "frozen" flow will occur.

   Some IBM-7090 calculations of the history of an isentropically expanding mixture of 78.33 per cent $CsNO_3$ and 21.67 per cent Al initially at 27.2 atm are presented. (None of the above-mentioned assumptions were made except the equilibrium assumption.)

Pressure (atm)	Temperature (°K)	Mole Per Cent Electrons	Velocity (cm/sec)
27.2	4428	1.55	0
1.0	3610	2.15	127,000
0.00052	2523	4.34	208,000
0.00007	2313 (Al_2O_3 solidifies)	4.76	221,000

The increase in electron fraction continues without reaching a maximum until the pressures reached are so low that thermodynamic equilibrium is surely not maintained. Thus the chamber conditions should represent a conservative estimate of electron output for units large enough so that heat loss to the walls is not excessive.

   In practice there is clearly no need for providing a supersonic expansion cone on the nozzle for isentropic expansion to the ambient pressure; on the contrary, a simple orifice minimizes heat loss from the exhaust stream

and reduces opportunities for deposit build-up. The emerging plume will undergo
an irreversible expansion, involving a shock pattern, until the ambient pressure
is reached. The final velocity will be lower and the final temperature higher
than for the isentropic expansion to the same pressure, so of course the final
equilibrium electron concentration will be higher for this reason.

The magnitude of the rate constant for dissociation during expansion
must be considered. The rate constant for cesium ion recombination has been
measured by various investigators at pressures from 10^{-3} to 1 mm Hg (6,7,8);
while the results for the second-order rate coefficient are not in agreement, they
may all be correlated empirically by the expression,

$$\alpha = 4.7 \times 10^{-5} \, p/T \qquad (cm^3/sec) \qquad (2)$$

where α is the recombination rate constant for

$$Cs \underset{\alpha}{\overset{\beta}{\rightleftharpoons}} Cs^+ + e$$
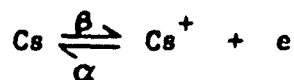
and p and T are expressed in mm Hg and °K respectively. Since the equilibrium
constant, equal to β/α , is known from thermodynamics to be

$$\beta/\alpha = 2.36 \times 10^{15} \, T^{3/2} \, 10^{-19,640/T} \qquad (cm^{-3}) \qquad (3)$$

the ionization rate constant β is readily calculated from equation (2) and (3).
(It should be remembered, however, that α as given by equation (2) may be quite
unreliable.) One actually wants the half-life of the ionization reaction, given
by $0.693/\beta$. Assuming expansion from 27.2 atm, we find that at 3000°K the pressure
has dropped to 11 mm Hg; at this condition the half-life for ionization as deter-
mined by the above procedure is 0.04 microseconds. On further expansion to 2500°K
and 0.38 mm Hg, the half-life is now much longer, 24 microseconds. Since the
flow rate is about 0.2 cm/microsecond and the expansion occurs in a distance of
the order of centimeters, these results imply that freezing of the ionization
reaction will occur between 2500 and 3000°K.

The foregoing argument must be viewed with skepticism not only because
of lack of precise ionization rate data, but also because two-phase flow is
involved, and the degree of equilibration between particle and gas is unknown.
If there were no energy exchange between particles and gas, the gas on expanding
to vacuum could cool to below room temperature, according to the isentropic law,
while the particles remained hot. This is clearly not the case, since the

expanded gas at 1 mm Hg is still hot enough so that the cesium vapor is emitting a line spectrum, the intensity of which implies temperatures well above 2000°K. Also the particle size is known to be very fine, a micron or less, and the solid-to-gas ratio is high, so substantial energy transfer would be expected during expansion. Nonetheless, no rigorous treatment of the problem is possible.

Once the pressure in the plume has equalized, further changes in electron concentration may occur because of radiant cooling of condensed particles or effects associated with mixing with ambient air, specifically cooling, dilution, and formation of O_2^-. Discussion of these effects is beyond the scope of this paper. At sufficient altitude the low collision rates will permit significant electron lifetime.

In summary, the cesium nitrate-aluminum electron generator should deliver a plasma to the upper atmosphere containing at least 0.86×10^{20} electrons per gram of charge (chamber conditions at 175 psi). The electrons per unit volume in the plume obviously depends on ambient pressure and plume temperature.

DESIGN AND OPERATING CHARACTERISTICS OF ELECTRON GENERATOR

To date, three sizes of cesium nitrate-aluminum electron generators have been developed and test-fired. Charge ignition is accomplished by a standard squib, and aluminized solid propellant is used as an aid. Generally, pressure peaks occur during charge ignition from simultaneous burning of the main charge and the ignition aid. This simultaneous burning has been found to be necessary for reliable charge ignition.

A typical chamber pressure vs. time plot for a test firing is shown in Figure 1. Both burning time and chamber pressure can be adjusted within limits by changing the nozzle throat diameter. Combustion performance is not as smooth as that of normal solid rocket propellants, but appears adequately steady for electron-generating purposes. Charge burning rates of 0.1 to 0.15 inches per second at 250 psi have been observed. Burning rate is somewhat controllable with selected inorganic additives. Pressure oscillations of approximately 5 to 6 cycles per second have been observed in the largest of the three units. These oscillations, which begin immediately after ignition and damp out during the first portion of the firing, are presently attributed to the behavior of molten aluminum oxide in contact with a relatively cold nozzle insert. No oscillations have been observed in the two smaller units.
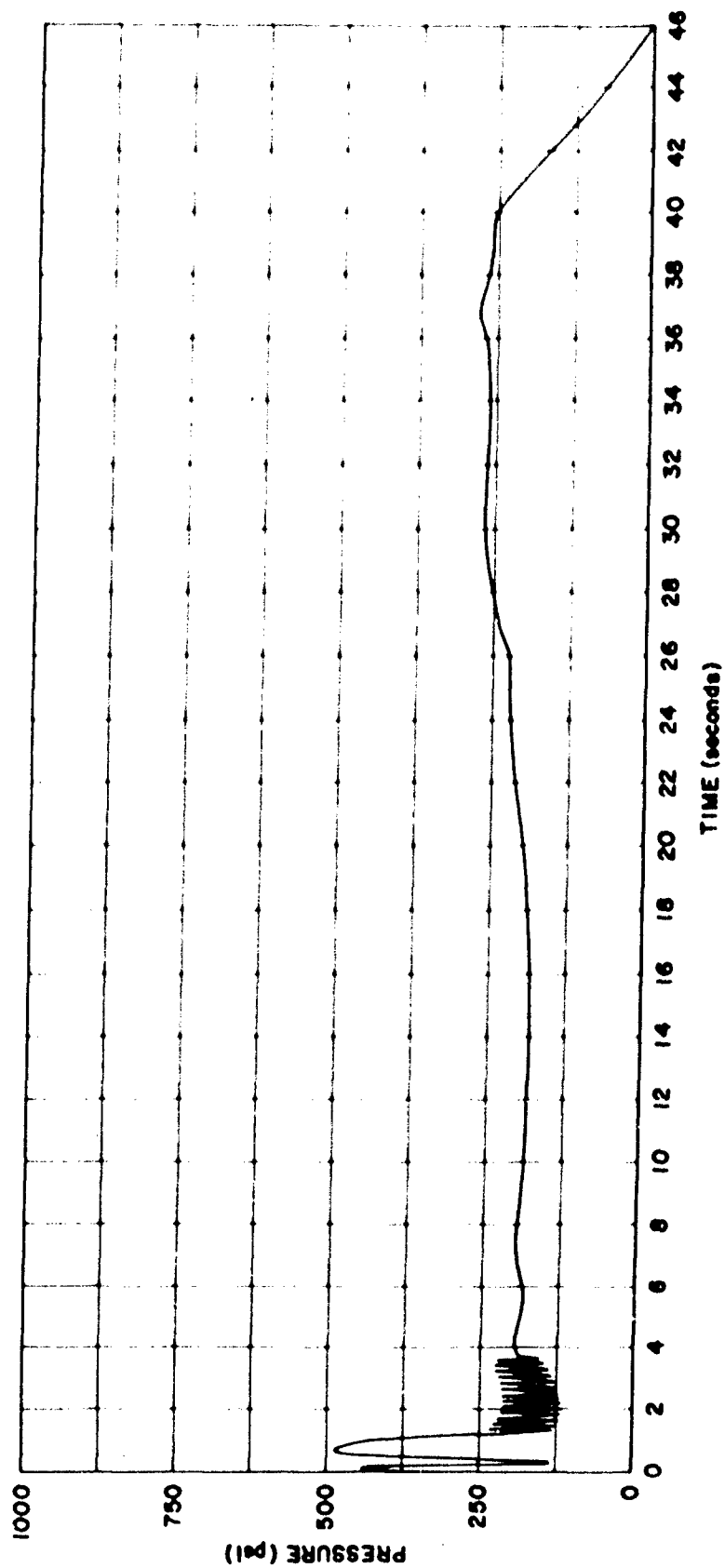
Figure 1. Typical Chamber Pressure vs. Time Curve for Firing of Electron Generator.

Further development work to improve burning characteristics and to refine hardware design is presently under way.

MEASUREMENTS OF ELECTRON YIELD

Two of the larger generators have been fired into an altitude chamber at the Naval Research Laboratory. Measurements of electron yield by microwave attenuation and spectrographic line-broadening techniques were made as described below.

A. Test Firing at One Mm Hg

This generator was equipped with a graphite nozzle of 0.220-inch throat. Pulsation occurred for three seconds after ignition, followed by 87 seconds of steady operation at 100 psi. The exhaust jet was deflected sideways from time to time by slag, as shown by a motion picture record. The visible structure of the plume is believed to be associated with the shock-wave pattern.

The microwave absorption apparatus of W. W. Balwanz (Naval Research Laboratory) was focussed on the geometric axis of the motor. The apparatus was mounted on a track allowing traversal along this axis. The instrument registered maximum absorption along the entire traversal length throughout the firing. This indicates that the frequency of the electromagnetic radiation impinging on the plasma was less than the plasma frequency. Since the instrument was operated at 54 kmc, this means that the electron density was greater than 3.6×10^{13}/cc.

An emission spectrum obtained with an instrument of about 35Å/mm dispersion gave no observable Stark-broadening of the cesium emission lines. Even with an instrument of higher dispersion no detectable broadening would have been expected at a pressure as low as one mm. However calculations showed that, by maintaining a higher ambient pressure and using a higher-dispersion spectrograph, Stark-broadening should be detectable, and should lead to a value of electron concentration.

B. Test Firing at 40 Mm Hg

This generator was equipped with a tungsten nozzle with 0.187-inch throat. The initial ambient pressure was 25 mm Hg, rising to ca. 40 mm Hg soon after ignition. Combustion duration was 41 seconds, with pulsation (5.8 cycles/sec) for the first eight seconds, at a mean chamber pressure of 220 psi, with subsequent

smoother burning at the same mean pressure until tailoff. A microwave absorption apparatus at 35 kmc located 91 cm downstream followed the 5.8- cycle pulsations, showing peak attenuations up to 7 db. This is close to the saturation of the instrument and corresponds to about 10^{13} electrons/cc.

A Bausch and Lomb 1.5-meter grating spectrograph with 10Å/mm dispersion, focussed 15 cm downstream of the exit plane, was set to receive the spectrum from 4500 to 6500Å. Figure 2 shows this spectrum with many broadened cesium emission lines. Widths of chosen lines were measured and compared with those calculated by Griem (9). The reliability of these calculations has recently been confirmed experimentally by Stone and Agnew (10).

In chosing an appropriate line for measurement it was found generally most reliable to work with isolated lines (preferably of the sharp, diffuse, or fundamental series) which were still observable above the background and which also corresponded to an upper-level quantum number as high as possible. This was done to insure optical thinness of the line; accurate line-width measurements with optically thick lines are at best very difficult to perform. Calculations and observations have shown that many of the lines corresponding to lower parent level quantum numbers are optically thick, if not reversed.

The spectrograph was aligned so that the light coming from a cross section of the plume, and in the plane of the cross section, passed through the slit. Thus an intensity profile of the plume was focussed along the length of the slit. Knowledge of the cross-sectional plume profile is necessary in order to use Abel inversion techniques to determine the intensity at the center. Actually an Abel inversion is performed at each of a series of wavelength positions covering the line under study so that an intensity profile as a function of wavelength characteristic of the plasma conditions in the center of the plume is obtained. It is the width at half maximum of this profile which is compared with the theoretical calculations used to determine the electron density.

The 5504Å ($11D_{5/2} \rightarrow 6P_{3/2}$), and 5257Å ($12D_{3/2} \rightarrow 6P_{1/2}$) lines were chosen for study and an Abel inversion performed on both. Assuming a plume temperature of 3000°K, the half-width measurements on these two lines yield values of 1.0×10^{15} and 0.6×10^{15} electrons/cc respectively. These values average to 0.8×10^{15} electrons/cc which is considered to be accurate to about
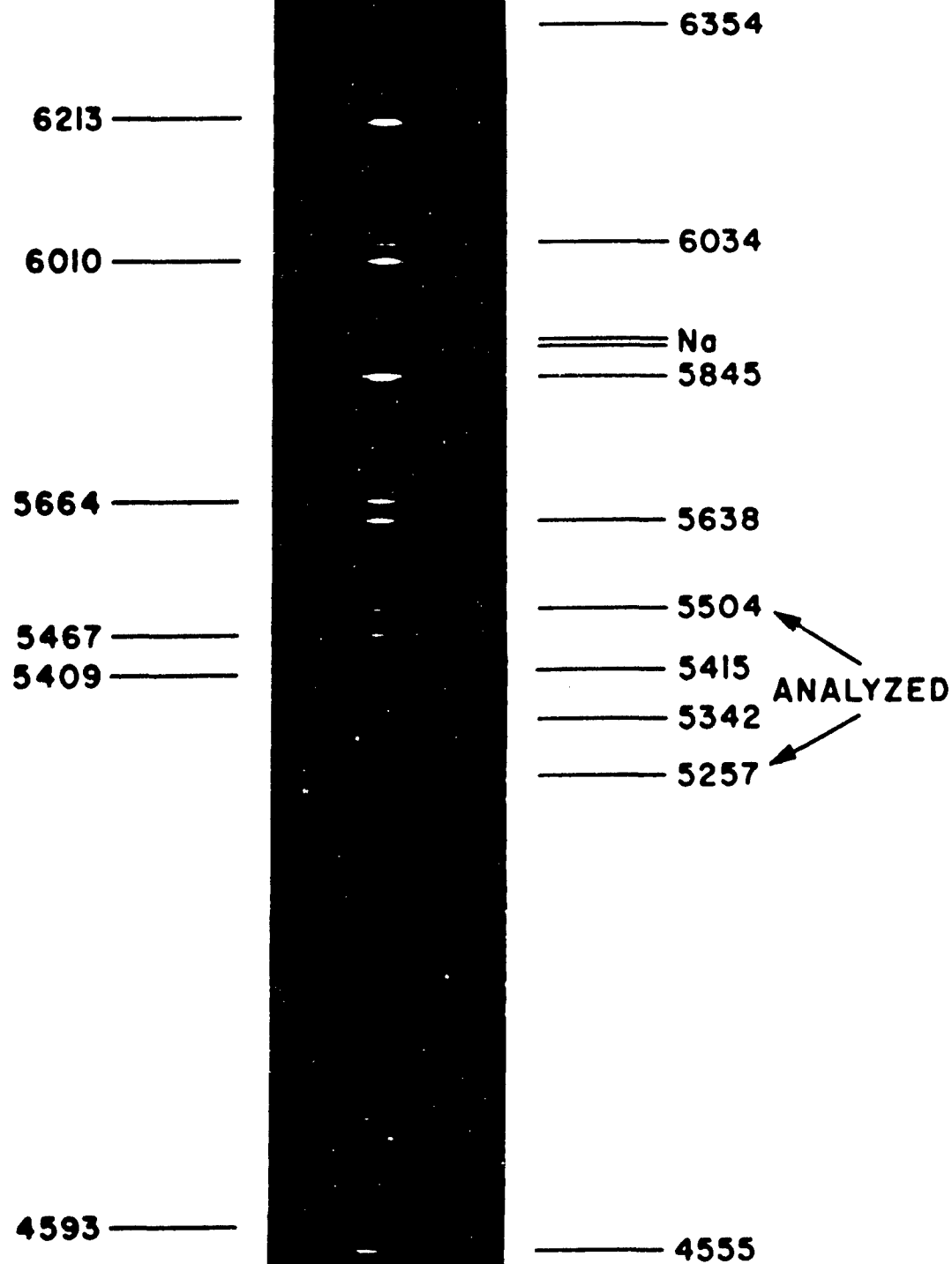
Figure 2. Spectrum of Plume at 40 mm Hg, 15 cm Downstream of Nozzle. Cesium Emission Lines are Labeled.

50 per cent. The method itself under the best experimental conditions is expected to be accurate to about 15 per cent. The increase in the estimated error is given because of the transient conditions and the high particulate background in the plume.

The vertical distance along the profile photograph was calibrated against vertical distance at the position of the plume profile, so that it was determined that the plume diameter at 15 cm downstream of the orifice was about 5.3 cm, where the limits are determined by the points at which about 10 per cent of the broadening at the center occurs.

The fact that a measurement of about 10^{15} electrons/cc was obtained at 15 cm downstream whereas at 91 cm the density had dropped to 10^{13} electrons per cc is probably indicative of considerable recombination or attachment along the length of the plume at this pressure. Less electron loss would be expected at 1 mm Hg.

The measured value of 0.8×10^{15} electrons/cc at 40 mm Hg may be compared with the following estimate. If the temperature in the plume is taken as roughly 3000°K, then at 40 mm Hg there are 1.3×10^{17} molecules and particles of all types per cc, according to the perfect gas law. If 2 per cent of these are electrons (cf. thermodynamic analysis of isentropic expansion), then 2.6×10^{15} electrons/cc would be expected. (If the plume temperature is 2000°K instead of 3000°K, then the predicted electron concentration comes out 3.9×10^{15}/cc.) The measured and calculated values are remarkably consistent when one considers that some electron loss by dilution and attachment must occur between the nozzle and a point 15 cm downstream, at this pressure.

REFERENCES

1. Marmo, F.F., Aschenbrand, L.M., and Pressman, J., ARS Journal, Vol. 30, 523-530 (1960).

2. Rosenberg, N.W. and Paulson, J.F., Chemical Reactions in the Lower and Upper Atmosphere. Interscience Publishers, New York. 1961, pp. 331-351.

3. Fagg, L.W. and Friedman, R., ARS Journal, Vol. 31, 157 (1961).

4. Nichol, J., Siminski, V., and Wolfhard, H.G., Eighth Symposium (International) on Combustion, Williams and Wilkins, Baltimore, pp. 235-241 1962.

5. Golomb, D., and Berger, A.W., Air Force Cambridge Research Laboratories Report 229, Geophysics Corporation of America, Jan. 1961.

6. Wada, J.Y. and Knechtli, R.C., Proceedings of the IRE, Dec. 1961, pp. 1926-31.

7. Mohler, F.L., J. Res. NBS, Vol. 19, 447-56 (1937).

8. Dandurand, P. and Holt, R.B., Physical Rev., Vol. 82, 278-9 (1951).

9. Griem, H.R., University of Maryland. In Press.

10. Stone, P.M. and Agnew, L., Phys. Rev., 127, 1157-62 (1962).